Original Research Article

Self-assembly of bioinspired catecholic cyclodextrin TiO$_2$ heterosupramolecule with high adsorption capacity and efficient visible-light photoactivity

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ABSTRACT

In this work, an efficient and simple supramolecular approach to introduce cyclodextrin on TiO$_2$ was demonstrated using the protocatechuic acid functionalized β-cyclodextrin (PCA-β-CD) that had a bioinspired catecholic structure. Two types of PCA-β-CD/TiO$_2$ heterosupramolecules were obtained through a facile dip coating of TiO$_2$ nanoparticles (Hombikat UV-100 and Fe$_3$O$_4$@SiO$_2$@TiO$_2$) in PCA-β-CD aqueous solution. The high surface coverage of Hombikat UV-100 or Fe$_3$O$_4$@SiO$_2$@TiO$_2$ by the attached PCA-β-CD was calculated to be 49.4% or 74.2% in the PCA-β-CD/TiO$_2$ based on the TGA results, and it was also confirmed by the optical properties study that PCA-β-CD located onto the TiO$_2$ surface mainly through the coordination of the catechol part on the cyclodextrin small ring side and TiO$_2$. Compared with the adsorption amount onto bare UV-100 and Fe$_3$O$_4$@SiO$_2$@TiO$_2$, the adsorption of bisphenol A onto PCA-β-CD/UV-100 and PCA-β-CD/Fe$_3$O$_4$@SiO$_2$@TiO$_2$ was 6.9 and 7.9 times higher, respectively, because of the high inclusion affinity between PCA-β-CD's cavity and bisphenol A. Moreover, the two PCA-β-CD/TiO$_2$ heterosupramolecules showed a high photoactivity to bisphenol A under light irradiation extending to the visible-light range. The cyclic use and X-ray photoelectron spectroscopy analysis results revealed that the PCA-β-CD layer in PCA-β-CD/TiO$_2$ was stable and that the catalyst possessed reusable properties.

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1. Introduction

Recently, the applications of nanomaterials have been enriched in the areas of sensors, molecular electronics, catalysts, dye-sensitized solar cells etc. by the formation of heterosupramolecular assemblies [1–3]. More importantly, nanomaterials can be endowed with the molecular recognition abilities after modification with host molecules including cyclodextrins (CDs), calixarenes and proteins [2,4–8]. The linked host molecules can act as a "bridge" between the guest molecules and the surface of the nanomaterial, which can lead to more guest-targeting and efficient functions of the nanomaterial.

Titanium dioxide (TiO$_2$), a well-known semiconductor, has been widely used as a photocatalyst in the environmental realm. The photodegradation of various organic pollutants, the photoreduction of inorganic contaminants and the inactivation of microorganisms have been performed with noteworthy results

[9–13]. Cyclodextrin modified TiO$_2$, a typical type of host-modified nanomaterial with the recognition ability, has attracted renewed interest since Willner and his colleagues observed that native β-CD could stabilize TiO$_2$ colloids and facilitate the interfacial electron transfer processes [14]. The β-CD/TiO$_2$ heterosupramolecule as well as nanowire can be easily obtained by the direct adsorption or photo-induced self-assembly of β-CD onto TiO$_2$ by the physisorption and/or H-bonding interactions between hydroxyl groups of β-CD and TiO$_2$ [7,15–17].

However, there are two shortcomings of the β-CD/TiO$_2$ heterosupramolecule that obstruct the development of its application. The first is the relatively low adsorption amount of β-CD onto TiO$_2$ for the weak interaction, like the maximum adsorption amount of the native β-CD onto Hombikat UV-100 and Degussa P25 were found to be only 33 μmol/g and 5 μmol/g [7,16]. On the one hand, the cyclodextrin attached on the surface TiO$_2$ can capture the photogenerated holes, which leads to the enhanced photoactivity of TiO$_2$. On the other hand, the strong inclusion affinity of the pollutants with attached cyclodextrin allows the pollutants to more easily contact the surface of the catalysts. Thus, the amount (the concentration) of cyclodextrin on the surface of TiO$_2$ is a critical factor in the photocatalytic performance of the β-CD/TiO$_2$ heterosupramolecule. Many attempts have been applied

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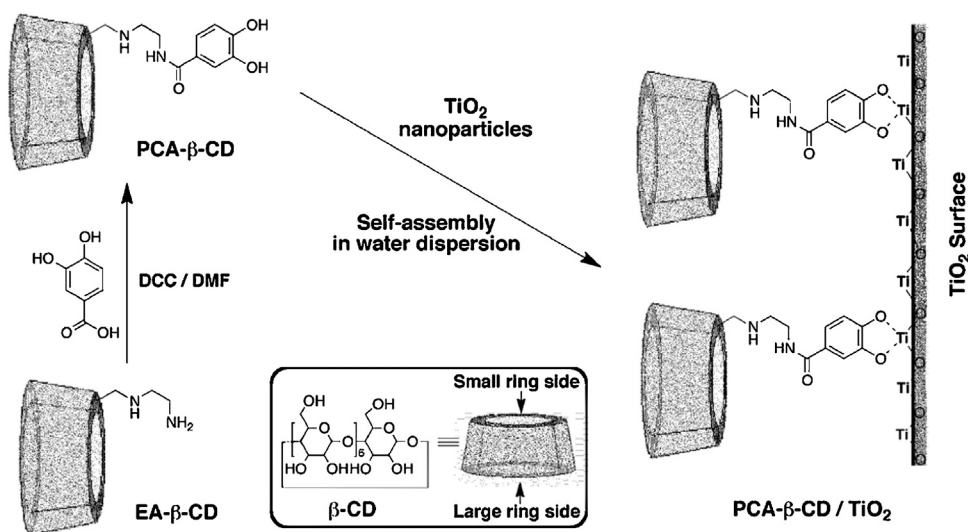
Scheme 1. The synthesis route of PCA-β-CD/TiO$_2$.

to increase the loading amount of cyclodextrin onto metal oxide particles. A common method is to have chemical reactions occur between the hydroxyl on the surface of the metal oxide particles and cyclodextrin (or its derivatives) or to use cross-linking agents, such as epoxides and halides [18–21]. In addition, photo-induced self-assembly is another method and incorporates the main advantage of cyclodextrin's high hole scavenging ability [15–17]. However, those reported strategies, especially the molecular synthesis method, are to some extent complicated and time consuming, and organic solvents are normally used during the reactions. The other shortcoming is the disadvantageous orientation of the adsorbed β-CD on the TiO$_2$. In an earlier report, we found that native β-CD located on the surface of TiO$_2$ predominately by its large ring side, which could cause the inhibition effect on the photodegradation of certain pollutants that could enter the cavity only from β-CD's large ring side [8]. It would thus be helpful to extend the applicability of β-CD/TiO$_2$ for more pollutants through controlling the orientation of adsorbed β-CD with an opening large ring side. In the recent decades, catechol and its derivatives were found to have high adsorption affinity for several metal oxide particles, including TiO$_2$, due to the formation of ligand–metal coordination bonding between the phenolic hydroxyl group in catechol and unsaturated Ti on the TiO$_2$ surface [22–25]. Moreover, since Lee reported the surface modification method using dopamine solution [26], which was inspired by the composition of adhesive proteins in mussels, the coating technique based on catecholic chemistry has aroused renewed interest for its simple realization, high loading amount and wide suitability [27]. In the present work, protocatechuic acid functionalized β-cyclodextrin (PCA-β-CD, shown in Scheme 1) was first synthesized. With its catecholic moiety, the PCA-β-CD can easily self-assemble on TiO$_2$, so the hetero-supramolecule of PCA-β-CD/TiO$_2$ was efficiently prepared through the facile dip coating of TiO$_2$ into an aqueous solution of PCA-β-CD. This self-assembly coating is much more facile than the previous molecular synthesis methods and is preformed in aqueous solution. The heterosupramolecule has the large ring side of cyclodextrin cavities open to the bulk solution phase of the pollutants [18–21]. Two types of TiO$_2$ (Hombikat UV-100, abbreviated as UV-100 and Fe$_3$O$_4$@SiO$_2$@TiO$_2$, abbreviated as m-TiO$_2$) were involved in this work, for the commercial UV-100 had a higher specific surface area and the self-made Fe$_3$O$_4$@SiO$_2$@TiO$_2$ could be easily magnetically separated. Both of the PCA-β-CD/TiO$_2$ heterosupramolecules showed promising adsorption capacity to BPA, the most common

endocrine disruptor, in water. PCA-β-CD/TiO$_2$ also presented high and reusable visible-light photoactivity to bisphenol A (BPA). The high visible-light induced activity indicates that PCA-β-CD/TiO$_2$ possesses great potential for harvesting solar energy for sewage treatment.

2. Materials and methods

2.1. Reagents

β-CD was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai), and was purified via recrystallization from water before use. Analytical grade 1,2-ethanediamine, triethylamine, dicyclohexylcarbodiimide (DCC), dimethylformamide (DMF), acetone and methanol were commercial products of Sinopharm Chemical Reagent Co., Ltd. (Shanghai). All of the solvents were dehydrated before use. Protocatechuic acid (PCA, ≥97%) was obtained from ALADDIN Reagent (Shanghai) Co., Ltd. Sephadex G-25 (pharmacia) was used as received. Hombikat UV-100 (Sachtleben Chemie GmbH) was used as received. Fe$_3$O$_4$@SiO$_2$@TiO$_2$ was a home-made TiO$_2$, and its characteristics have been documented [28].

2.2. Synthesis of PCA-β-CD

Mono [6-ethylenediamino-6-deoxy]-β-cyclodextrin (EA-β-CD, 2 mmol), which was synthesized according to the reported procedures [29], was dissolved in DMF (50 mL) containing protocatechuic acid (PCA, 2 mmol), dicyclohexylcarbodiimide (2.4 mmol) and two drops of triethylamine below 5 °C. The resultant mixture was stirred for 1 day in an ice bath and then for an additional 2 days at room temperature. The reaction mixture was evaporated under reduced pressure to dryness. The residue was dissolved in water, and the resultant solution was poured into acetone to give a precipitate. The crude product obtained was collected by filtration and purified by column chromatography over Sephadex G-25 with distilled deionized water as an eluent to give the pure PCA-β-CD. Yield: 61%. ^{1}H NMR data: (400 MHz, D$_2$O, ppm): δ 7.293 (s, 1H, H of aromatic ring), δ 7.245 (d, 1H, H of aromatic ring), δ 6.775 (d, 1H, H of aromatic ring), δ 4.940 (s, 7H, H of C-1 of cyclodextrin), δ 3.0–4.0 (m, 42H, H of C-2–C-6 of cyclodextrin), δ 2.5–3.0 (m, 4H,

H of methylene). FTIR (KBr): ν 3407, 2928, 1657, 1550, 1380, 1284, 1155, 1081, 1031, 942, 847, 607 cm^{-1}.

2.3. Self-assembly coating TiO$_2$ with PCA-β-CD

Two-hundred micromolar PCA-β-CD was added to the 1.0 g/L TiO$_2$ (UV-100 or m-TiO$_2$) water dispersion. Then, the dispersion was stirred violently on a mechanical stirrer for 10 min in the dark. The suspended solution was centrifuged, and the solid phase was carefully washed with ultrapure water until no PCA-β-CD was detected in the supernatant liquid. The PCA-β-CD/TiO$_2$ hybrid nanoparticles were dried under dynamic vacuum at 50 °C for 12 h. FTIR (KBr): ν 3404, 2926, 1634, 1381, 1282, 1153, 1080, 1031, 536 cm^{-1}. β-CD/UV-100 was obtained using a light induced self-assembly method according to the previous report and used as a reference material in this work [16].

2.4. Characterization of PCA-β-CD/TiO$_2$

The Brunauer–Emmett–Teller (BET) surface areas of the two TiO$_2$ were determined using a Micromeritics ASAP 2020 setup. Thermo gravimetric analysis (TGA) was conducted on a TGA 2050 thermogravimetric analyzer with a heating rate of 10 °C/min from 50 °C to 800 °C under a nitrogen atmosphere. FT-IR spectra of sample pellets with KBr were recorded on a Nicolet 5700 Fourier transform infrared (FTIR) spectrometer (Thermo Electron Corporation, American). UV–vis diffuse reflectance spectra were recorded on a Shimadzu 2550 UV–vis spectrophotometer, with BaSO$_4$ as the background between 300 and 800 nm. Scanning electron micrographs (SEM) were taken with a FEI-QUANTA 200 microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy images were, respectively, obtained on a JEOL JEM 2010HT and JEOL JEM 2010FEF microscope (Japan Electronics, Japan) at an accelerating voltage
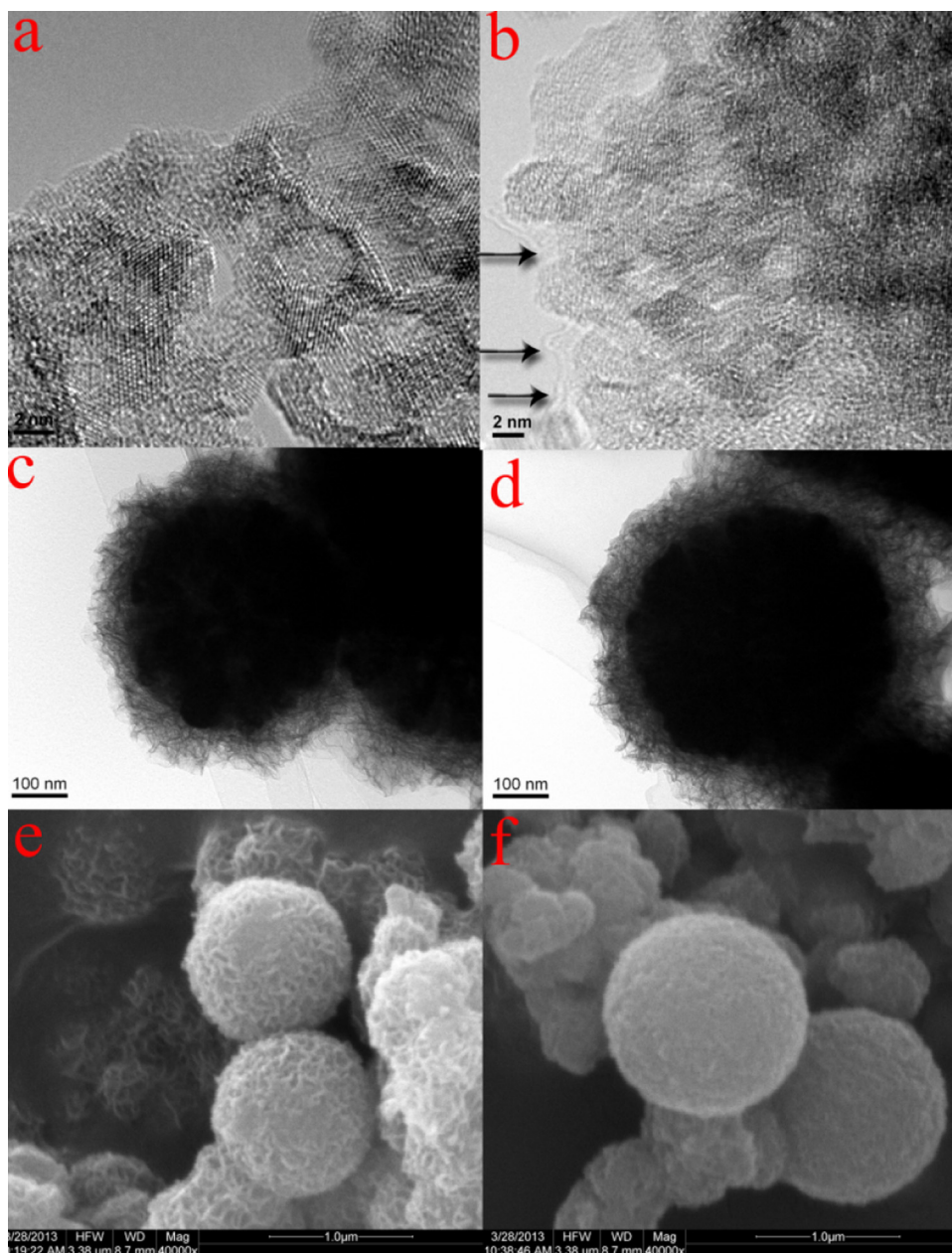

Fig. 1. Typical TEM micrographs of bare UV-100 (a) and PCA-β-CD/UV-100 (b), m-TiO$_2$ (c) and PCA-β-CD/m-TiO$_2$ (d). SEM micrographs of bare m-TiO$_2$ (e) and PCA-β-CD/m-TiO$_2$ (f).

of 200 kV. The X-ray photoelectron spectroscopy (XPS) analysis of PCA-β-CD/UV-100 before and after 12 h irradiation was performed on a Kratos XSAM 800 X-ray photoelectron spectrometer operated in FRR mode using nonmonochromatic Mg Kα (1253.6 eV) radiation. The applied voltage and current were 11.7 kV and 17 mA. The peak curve fitting was accomplished using the XPS peak 4.1 software.

2.5. Adsorption and degradation of BPA onto PCA-β-CD/TiO₂

The adsorption studies were performed in the dark using aqueous suspensions containing 20 μM BPA and 1.0 g/L PCA-β-CD/TiO₂. The 50 ml suspension in the 100 ml glass vessels was continuously stirred by using a constant temperature mechanical stirrer. During all adsorption process, 2 ml aliquots were collected at selected time intervals and were centrifuged and used for concentration determination. The experimental details for the degradation of BPA were described in our previous work, and the irradiation light ($\lambda \geq 420$ nm) intensity was 226 W/m² [8]. The concentration of BPA was determined by HPLC through a standard working curve from 0 μM to 25 μM. The mobile phase was a mixture of methanol/water (70/30, v/v) with a flow rate of 1 ml/min. The detection wavelength was 280 nm. The adsorption and photodegradaition of BPA over β-CD/UV-100 were also investigated to compare the performance of cyclodextrin modified TiO₂ obtained using different method.

3. Results and discussion

3.1. Morphological analysis of PCA-β-CD/TiO₂

The electron microscope is a powerful and intuitive technique for investigating the morphological character of nanoparticles. From the high-resolution TEM micrographs of PCA-β-CD/UV-100, it could be clearly observed that the outer surface of UV-100 was capped by an amorphous coating, which usually corresponded to a certain organic material (arrow pointed). Moreover, the "carbohydrate" coating was approximately 1–1.5 nm in thickness, which was very close to the PCA-β-CD height profile. For PCA-β-CD/m-TiO₂, comparing the TEM imagines shown in Fig. 1c and d, the TiO₂ layer became more compact after the modification with PCA-β-CD, whereas the magnetic core had no change. m-TiO₂ had a larger size and greater coverage rate with PCA-β-CD than did UV-100, so a more obvious and representative morphological change of TiO₂ came from the SEM micrographs of m-TiO₂ vs. PCA-β-CD/m-TiO₂. The significant difference was observed before and after introducing PCA-β-CD molecules: the surface of the resultant heterosupramolecule was much smoother than that of the bare m-TiO₂, which indicated that uniform coatings formed during the assembly process.

The results of the TEM and SEM indicated that PCA-β-CD was attached to the TiO₂ surface and that assembly behaviour resulted in morphological changes of TiO₂ by the formation of the cyclodextrin coating.

3.2. The loading amount of PCA-β-CD in PCA-β-CD/TiO₂ heterosupramolecules

The mono substituted PCA-β-CD with a definite structure was adopted in the surface modification of TiO₂. Cyclodextrin with a definite structure can form a complex with the surface metal atom of nanoparticle and produce a clear chemical composition of the heterosupramolecule, which allows the loading amount of cyclodextrin to be directly calculated from the TGA analysis of the heterosupramolecule. The loaded PCA-β-CD in PCA-β-CD/m-TiO₂ and PCA-β-CD/UV-100 were recovered from the TGA analysis
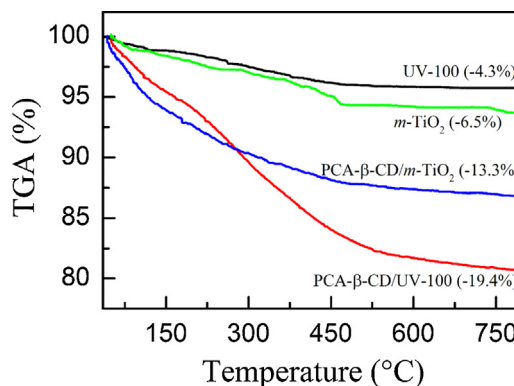

Fig. 2. TGA curves of UV-100 (black), m-TiO₂ (green), PCA-β-CD/m-TiO₂ (blue) and PCA-β-CD/UV-100 (red); the weight loss percentage of the sample shown in the parentheses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

(Fig. 2). The relatively higher weight loss for the PCA-β-CD modified TiO₂ than for the bare TiO₂ was due to the decomposition of the attached PCA-β-CD. From the TGA results, the amount of PCA-β-CD grafted on the UV-100 and m-TiO₂ could be calculated as 116 μmol/g (150 mg/g) and 54 μmol/g (70 mg/g), respectively.

The adsorption spectra of the PCA-β-CD before and after the interaction with UV-100 are shown in Fig. S1 (Supporting Information). The intensity of the absorption peaks of the protocatechuic acid amide part of PCA-β-CD in bulk solution decreased sharply after its interaction with the UV-100 suspension that processes the high BET surface area. The decrease revealed that a large amount of PCA-β-CD was located on the UV-100 surface from the bulk solution. A similar phenomenon also occurred when PCA-β-CD and m-TiO₂ were mixed in water. Based on the Beer–Lambert law, the loading amounts for PCA-β-CD onto UV-100 and m-TiO₂ were 136 μmol/g (176 mg/g) and 57 μmol/g (74 mg/g), respectively. Those results corresponded to the loading amounts of PCA-β-CD in PCA-β-CD/TiO₂ recovered from the TGA experiments.

Knowing that the BET surface areas for the UV-100 and m-TiO₂ are, respectively, 304 m²/g and 80 m²/g (Fig. S2, Supporting Information) and that the calculated area for the 1 μmol β-CD moiety is 1.1 m², the coverages of the UV-100 and m-TiO₂ surface by attached PCA-β-CD were calculated to be 49.4% and 74.2%, based on the cyclodextrin loading amount from the TGA results. The results indicated that most of the TiO₂'s surface, particularly for m-TiO₂, was covered by PCA-β-CD, which also suggested that only the guests that have high inclusion ability with PCA-β-CD could attach to the surface of TiO₂ through the cavity of PCA-β-CD.

3.3. FTIR of PCA-β-CD/TiO₂

The results from the IR spectrum further confirmed that PAC-β-CD has a strong co-relationship with TiO₂. In the IR spectrum of the bare UV-100 (Fig. 3), a broad absorption band centred around 3400 cm⁻¹, which was for the valence vibration of OH and two narrow peaks around 1631 cm⁻¹ and 1385 cm⁻¹ belonged to the deformation vibrations of the adsorbed water and the in-plane angular deformation of the surface OH groups, respectively [30,31]. When PAC-β-CD was located onto the UV-100, new peaks corresponding to PAC-β-CD were registered. The absorption peak at 1282 cm⁻¹ responded to the deformation vibrations of the aryl oxygen parts on PAC-β-CD, and the peak around 2926 cm⁻¹ and the peaks in the region 1000 cm⁻¹ to 1200 cm⁻¹ were associated with the absorption for the cyclodextrin ring part (the absorption peak at 2926 cm⁻¹ was assigned to the asymmetric and symmetric CH and CH₂ valence vibrations; the absorption peaks at 1153, 1080, 1031 cm⁻¹ were assigned to the valence vibrations of the C—O—C
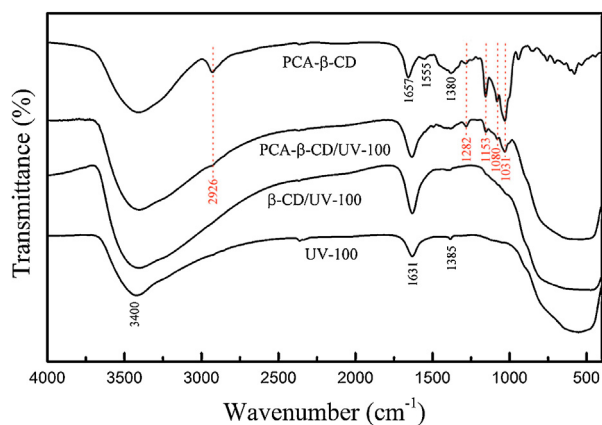
Fig. 3. FTIR of PCA-β-CD, bare UV-100, β-CD/UV-100 and PCA-β-CD/UV-100.

and C—O bonds in the ether and hydroxyl groups of cyclodextrin) [32]. Conversely, when native β-CD was attached to the UV-100, no obvious new peaks from the β-CD part in the β-CD/UV-100 could be found, considering the relatively little amount of β-CD in β-CD/UV-100 [16].

3.4. Optical properties of PCA-β-CD/TiO₂

Comparing the structures of native β-CD and PCA-β-CD, their affinity difference to TiO₂ should be from the substituent at the small-ring side of the β-CD cavity. In other words, the substituent group of β-CD ought to have a much stronger coordination to the TiO₂ surface than the hydroxyl groups in the β-CD ring. It was reported that the TiO₂ nanoparticle had the ability to form a charge transfer complex with the catechol bidentate ligand and that it resulted in a significant change in the TiO₂ optical properties. When PCA-β-CD and UV-100 were mixed in water, the white UV-100 suspension became yellow (vial b in the inset of Fig. 4), which was visual evidence for the coordination of the surface Ti atoms of UV-100 with the catechol part of PCA-β-CD. The absorption properties of PCA-β-CD/UV-100 solid, using bare UV-100, PCA-β-CD and native β-CD/UV-100 solids as references, are also presented in Fig. 4. The visible absorption intensity of the PCA-β-CD/UV-100 nanoparticle (curve b) was much higher than that of bare UV-100 (curve c), whereas β-CD/UV-100 (curve d) had similar absorption properties as UV-100 (curve c) because of the relatively low loading amount of β-CD. The absorption bands in the visible region observed in the catechol modified TiO₂ correspond to ligand to metal charge transfer and the stoichiometric ratio for Ti atoms to the modifier catechol in the charge transfer complexes was 2:1
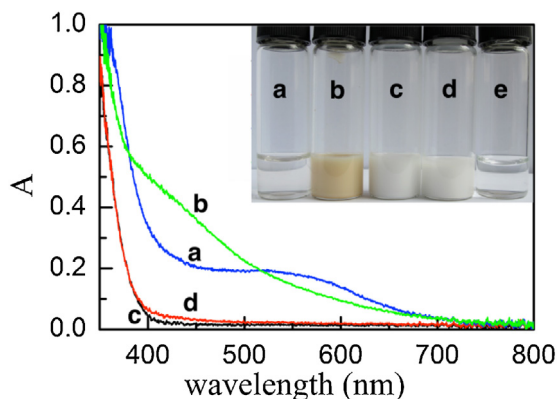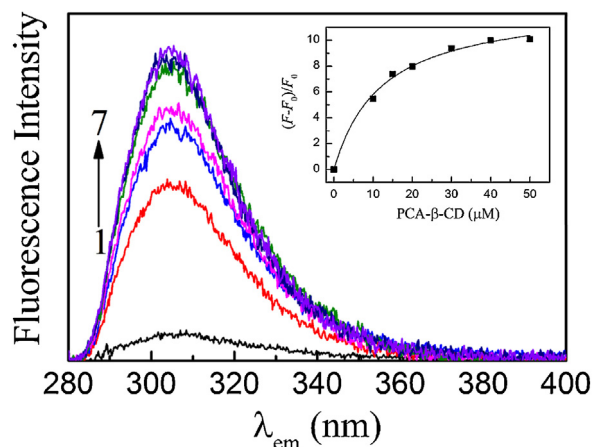

Fig. 5. Effect of PCA-β-CD concentration on the fluorescence emission spectrum of BPA, PCA-β-CD: 0 μM (1), 10 μM (2), 15 μM (3), 20 μM (4), 30 μM (5), 40 μM (6), 70 μM (7), inset: Dependence of the fluorescence intensity at 305 nm for BPA with the concentration of PCA-β-CD. BPA = 10 μM, λ_{ex} = 260 nm.

[22–25]. Because PCA-β-CD is a type of substituted catechol, it is reasonable to propose that the absorption in the visible region for PCA-β-CD/UV-100 was caused by the ligand to metal charge transfer between PCA-β-CD and the Ti^{IV} located in an octahedral unsaturated coordination environment, as well as the reported catechol modified catalysts [22–25]. Therefore, the cyclodextrin part in PCA-β-CD/TiO₂ was attached onto the surface of TiO₂ predominately by the small ring side, which was opposite to the native β-CD [8].

3.5. Inclusion of BPA with PCA-β-CD

The inclusion behaviour of BPA with PCA-β-CD was investigated using stationary fluorescence spectroscopy. A substantial increase was observed for the fluorescence intensity when BPA was bound to PCA-β-CD (Fig. 5).

A good linear fit of the experimental data to the Benesi-Hildebrand formula indicated that BPA formed a 1:1 inclusion complex with PCA-β-CD. The binding constant was $8.2 \times 10^4 \, M^{-1}$ (Fig. 5, insert), which was relatively larger than that of BPA with β-CD ($7.0 \times 10^4 \, M^{-1}$). The large inclusion constant indicated that BPA could be easily attached to TiO₂'s surface through the cavity of PCA-β-CD, which will be studied later.

3.6. Adsorption of BPA onto PCA-β-CD/TiO₂

The adsorption of BPA onto two types of PCA-β-CD/TiO₂ reached equilibrium within 30 min (Fig. S3, supporting Information). The equilibrium adsorption amounts were 11.0 and 7.1 μmol/g, respectively. On the other side, the equilibrium adsorption amounts of BPA on bare UV-100 and m-TiO₂ were only found to be 1.6 and 0.9 μmol/g, respectively (Fig. S4, Supporting Information). The main reason for the increased adsorption was that the attached PCA-β-CD could offer more attractive adsorption sites due to its high inclusion ability with BPA.

The adsorption of BPA over PCA-β-CD/TiO₂ fitted the Langmuir isotherm well (Fig. 6), which also indicated that BPA could adsorb in the attached PCA-β-CD monolayer. The calculated maximum adsorption amount over PCA-β-CD/UV-100 and PCA-β-CD/m-TiO₂ were 24.5 and 19.6 μmol/g, respectively. In contrast to the high occupation of carboxymethyl-β-CD linked to a magnetic TiO₂ surface by either bisphenol A (87%) or dibutyl phthalate (72%) [18], only 21% and 36% of the cavities of adsorbed PCA-β-CD over UV-100 and m-TiO₂ were occupied by BPA, assuming that all of the

Fig. 4. UV–vis DRS of PCA-β-CD (a), PCA-β-CD UV-100 (b), UV-100 (c) and β-CD/UV-100 (d); and the images of samples (a), (b), (c), (d) and β-CD (e) aqueous solutions.
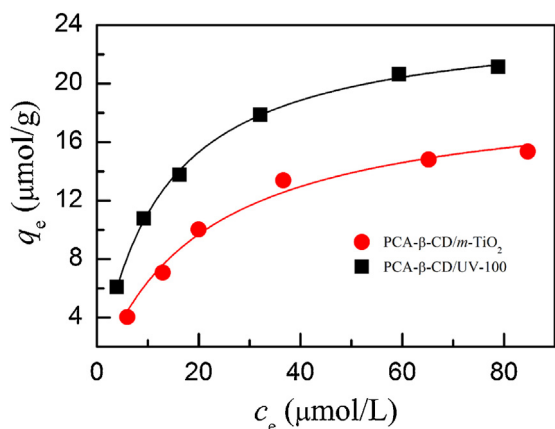
Fig. 6. Dependence of the adsorbed BPA per gram PCA-β-CD/TiO$_2$ (q_e) with the equilibrium concentration (c_e). The solid lines correspond to the fits of the data to the Langmuir adsorption isotherm model.

adsorbed BPA was in the cavity of PCA-β-CD in this work. The different occupation ratios of the anchored cyclodextrin were probably caused by the different load amounts of cyclodextrin and/or the different inclusion affinity of BPA with cyclodextrins in different micro environments. Moreover, the different dispersion behaviours of these photocatalysts would also contribute to the different occupation ratio.

3.7. Visible-light induced photodegradation of BPA over PCA-β-CD/TiO$_2$

As shown in Fig. 7, after reaching adsorption equilibrium in the dark for 30 min, the concentration of BPA decreased constantly over the two types of PCA-β-CD/TiO$_2$ heterosupramolecules under visible-light irradiation (Fig. 7). Further simulation showed the degradation of BPA over PCA-β-CD/TiO$_2$ followed a first-order kinetic mode. The observed kinetic constant k_{obs} (min^{-1}) for the degradation of BPA over PCA-β-CD/UV-100, PCA-β-CD/m-TiO$_2$ and β-CD/UV-100 were 0.012, 0.005 and 0.004, respectively. Compared with the results of the removal of BPA over PCA-β-CD/UV-100, β-CD/UV-100 that synthesized through a photo-induced self-assembly method had much lower activity [16]. The adsorption and photodegradation of BPA over β-CD/UV-100 were, respectively, 8 times and 2 times smaller than that of PCA-β-CD/UV-100. The differences in adsorption and photodegradation were likely
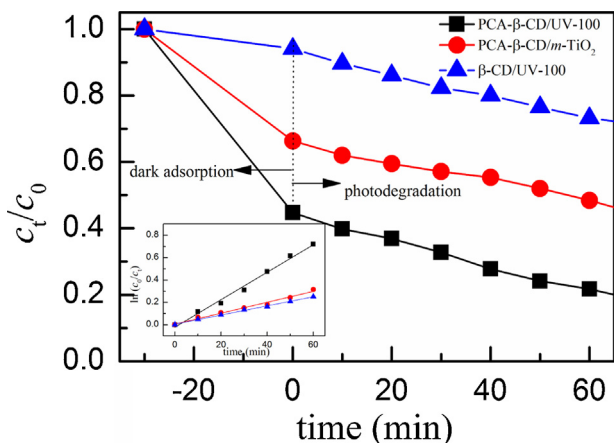

Fig. 7. Photodegradation of BPA over PCA-β-CD/TiO$_2$ and β-CD/UV-100 under visible-light irradiation ($\lambda \geq 420$ nm), inset: photodegradation kinetics fit of BPA over photocatalysts to the first-order kinetic mode. BPA = 20 μM, PCA-β-CD/TiO$_2$ = 1.0 g/L, β-CD/UV-100 = 1.0 g/L.
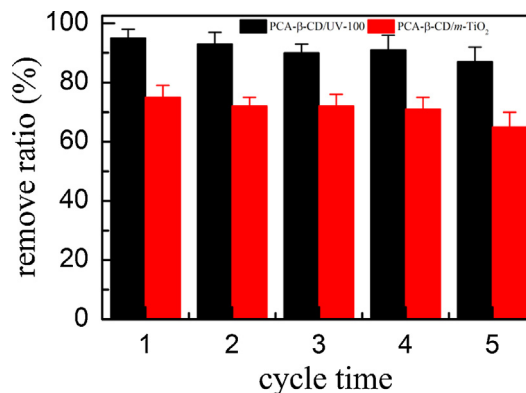

Fig. 8. Cyclic efficiency of the two PCA-β-CD/TiO$_2$ for the photocatalytic degradation of BPA aqueous solution under 120 min visible-light ($\lambda \geq 420$ nm) irradiation.

generated from the different loading amount over TiO$_2$ of PCA-β-CD and natural β-CD. No degradation of BPA occurred when bare TiO$_2$ was applied as the photocatalyst under visible irradiation (Fig. S5, Supporting Information).

The charge transfer complex between the catechol part and TiO$_2$ was formed during the self-assembly process of PCA-β-CD/TiO$_2$. The superoxide ion radical (O$_2$•$^-$) was generated when the charge transfer complex was irradiated under visible-light [33,34], and was found to be the predominant reactive oxygen species in the visible-light irradiated cyclodextrin/TiO$_2$ system [31]. Moreover, cyclodextrin derivatives were used to improve the efficiency of O$_2$•$^-$ trapping using various nitrones as scavengers [35–37], and the reaction between β-CD and diffusion mediated O$_2$•$^-$ could be neglected. Therefore, the overall visible-light degradation of BPA over the PCA-β-CD/TiO$_2$ heterosupramolecule could be accelerated because of the significantly increased loading amount of cyclodextrin.

3.8. Photo stability of PCA-β-CD/TiO$_2$

Sequential photodegradation experiments were performed to test the catalyst stability. As shown in Fig. 8, the decreasing trend in the final degradation efficiency was less than 10% after 5 repetitive experiments for PCA-β-CD/TiO$_2$. This result showed that PCA-β-CD/TiO$_2$ possesses great potential to be an effective and stable catalyst.

XPS experiments were performed to confirm the stability of the PCA-β-CD/TiO$_2$ and the results are shown in Fig. 9 and Figs. S6–S8 (Supporting Information). The binding energy of the Ti 2p region has no obvious shift, except the intensity has a slight change (Fig. S6), which indicates that no new chemical species of Ti were generated after either modification or irradiation. A new peak appeared in the O1s region after modification by PCA-β-CD (Fig. S7); analogous results have been obtained for the natural β-CD modified anatase TiO$_2$ [16,31]. Moreover, the new peak barely changed after 12 h of irradiation, which suggested that the monolayer was stable. As presented in Fig. 9 and Fig. S8, there were two inorganic oxygen species in bare UV-100: the Ti-O bond in the condensed phase and the surface hydroxyl. Two more organic contributions were obtained both in freshly synthesized and irradiated PCA-β-CD/UV-100 in addition to the inorganic oxygen species. The organic oxygen species accounted for 23.6% and 22.6% of the total oxygen species before and after irradiation, which implied that the linked PCA-β-CD had no obvious decomposition and further confirmed the photostability of PCA-β-CD/TiO$_2$. Actually, cylodextrin-TiO$_2$ wires could be obtained through a UV induced or solar light induced self-assembly process [15,17], which suggested that the cyclodextrin derivate were stable over TiO$_2$ surface. Du et al. suggested that the
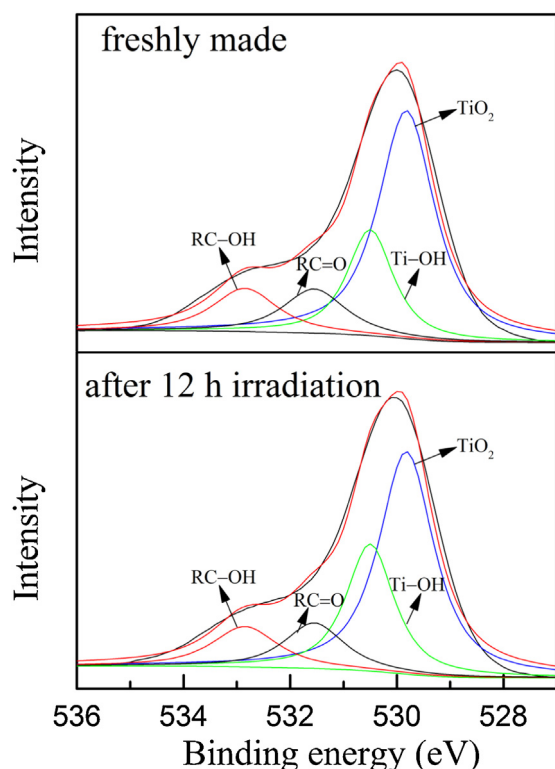
Fig. 9. High resolution XPS spectra of the O1s region for PCA-β-CD/UV-100 before and after irradiation.

probability of cyclodextrin desorption from TiO_2 decreases roughly exponentially with the number of glucose units in the cyclodextrins based on the first-principles calculations for the photo-oxidation of glucose, although a few transient C=C and C=O bonds are formed during the irradiation [38]. It was also noticeable that the ratio of organic oxygen species in PCA-β-CD/UV-100 was 1.4 times higher than the ratio in β-CD/TiO_2 (17.4%) obtained from the light induced self-assembly process [16]. This result indicated that the synthesis method reported in this work was simple and effective for obtaining heterogeneous supramolecules with high cyclodextrin loaded amounts.

4. Conclusions

PCA-β-CD/TiO_2 heterosupramolecules were easily obtained through a facile dip coating of TiO_2 into an aqueous solution of PCA-β-CD. Various techniques were utilized to characterize the functional nanoparticles. Most importantly, it was verified that PCA-β-CD/TiO_2 could efficiently adsorb and decompose pollutants, such as BPA, under visible-light because of the high capacity of cyclodextrin in PCA-β-CD/TiO_2. Our work demonstrated an efficient and facile supramolecular approach to introduce cyclodextrin onto TiO_2, and it could provide an easy way to obtain cyclodextrin modified metal oxide particles on a large scale to adopt this catecholic cyclodextrin. These easily made and high cyclodextrin-content heterosupramolecules, especially the magnetic PCA-β-CD/TiO_2, could be further applied in various fields, such as drug carriers, chiralseparators, or biosensors.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.11.002.

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